APPENDIX J

BACKGROUND SOIL AND GROUND WATER CONCENTRATIONS OF NATIVE ELEMENTS

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THE SOIL CHEMISTRY OF HAZARDOUS MATERIALS

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Element Fixation in Soil

INTRODUCTION

The inorganic fraction of soil is comprised of numerous sparingly soluble inorganic chemicals known as minerals. Soil minerals are products of an extremely complex chain of events involving the action of weathering, topography, and biota on a parent geologic material over some period of time. In general, minerals form in soil via three processes. First, soil minerals are derived from the physical disintegration of minerals originally present in the soil or by the physical disintegration of minerals deposited at the site by geological processes. Second, soil minerals are derived from the chemical transformation of minerals that are susceptible to weathering into those that are resistant to weathering. Third, soil minerals are formed via the subsequent precipitation of water-soluble elements which are released during the first and second processes. The first and second processes have a negligible impact on the ultimate fate of an element added to soil; however, the third has a major impact on an element's ultimate fate in soil.

Fixation refers to the soil chemical reactions which immobilize an element within the structure of a mineral or at the mineral surface. There are three types of fixation reactions. First, chemisorption is the formation of a covalent bond between an adsorbed element and a mineral surface which results in element immobilization. Second, solid state diffusion refers to the irreversible penetration of an element into the pore spaces of a mineral's structure. Third, precipitation refers to the formation of an insoluble solid comprised of elements which were previously dissolved in water.

The fixation of elements by soil minerals is very similar to the fixation, stabilization, or solidification methods utilized for some types of hazardous wastes containing metals. On the other hand, fixation of elements by soil minerals is unlike encapsulation, which encapsulates the metal within an insoluble, impermeable shell. In the waste fixation process, binders or fixatives such as fly-ash, soluble silicates, calcium and sulfur compositions, and cements and concretes are mixed with a hazardous waste. The fixative dissolves and releases anions which react with the metals to form precipitation products. Stabilized wastes are produced if the metal is "grafted" into an insoluble crystalline structure with the fixative via strong chemical bonds. A stable, fixed waste will bind and hold metals under natural environmental conditions. Likewise, fixation in soils should bind and hold elements under natural environmental conditions.

Relatively little is known about the first two types of soil mineral fixation reactions discussed above. However, these are not considered to be extensively occurring reactions. On the other hand, the fixation of elements via incorporation into the structure of soil minerals during mineral precipitation is an extremely important reaction. This chapter will focus on the types and amounts of elements found in soil, how these elements are fixed into mineral structures, and how some remedial actions have utilized element fixation.

ELEMENT CONCENTRATIONS IN SOIL

Eleven of the elements listed in Table 3.1, along with carbon, hydrogen, and oxygen, constitute over 99 percent of the total elemental content of soil: Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, and Ti. The remaining one percent is comprised of elements known commonly as the "trace elements." The word "trace" identifies the fact that they occur in soil in minute amounts; it has no bearing or relationship to any concentration limit protecting human health or biota.

Table 3.1 lists the mean concentrations, typical ranges, and observed limits of several elements in natural soil (i.e. background concentrations). The total concentration of any element, C_{Total}, in a soil is equal to:

$$C_{Total} = C_{Fixed} + C_{Adsorbed} + C_{Water} \tag{3.1}$$

where:

C_{Fixed} = concentration of fixed element comprising part of the structure of clay and soil minerals, in mg element/kg soil.

$C_{Adsorbed}$ = concentration of element adsorbed onto the surface of soil minerals and onto organic matter exchange sites, in mg element/kg soil.

C_{Water} = concentration of element in soil water or groundwater in equilibrium with $C_{Adsorbed}$, in mg soluble element/kg soil. (See Table 3.2 for natural background levels found in groundwater).

C_{Fixed} represents the "immobile" fraction of C_{Total}. The sum of $C_{Adsorbed}$ and C_{Water} represents the potentially mobile portion of C_{Total}; these will be discussed in detail in the next chapter.

There are four important facts that should be understood concerning the data listed in Table 3.1, the parameters listed in Equation 3.1, and the interrelationships of these parameters. First, C_{Total} should not be expected to be uniform with depth. Natural processes involved in the distribution of elements in the soil profile include:

TABLE 3.1 Native Soil Concentrations of Various Elements

Element	Concentration (ppm) Typical Range	Extreme Limits
Ag	0.1 - 5.0	0.1 - 50
Al	10,000 - 300,000	—
As	1.0 - 40	0.1 - 500
B	2.0 - 130	0.1 - 3000
Ba	100 - 3500	10 - 10,000
Be	0.1 - 40	0.1 - 100
Br	1.0 - 10	—
Ca	100 - 400,000	—
Cd	0.01 - 7.0	0.01 - 45
Ce	30 - 50	—
Cl	10 - 100	—
Co	1.0 - 40	0.01 - 500
Cr	5.0 - 3000	0.5 - 10,000
Cs	0.3 - 25	—
Cu	2.0 - 100	0.1 - 14,000
F	30 - 300	—
Fe	7,000 - 550,000	—
Ga	0.4 - 300	—
Ge	1.0 - 50	—
Hg	0.01 - 0.08	—
I	0.1 - 40	—
K	400 - 30,000	—
La	1.0 - 5000	—
Li	7.0 - 200	1.0 - 3000
Mg	600 - 6000	—
Mn	100 - 4000	1.0 - 70,000
Mo	0.2 - 5.0	0.1 - 400
Na	750 - 7500	400 - 30,000
Ni	5.0 - 1000	0.8 - 6200
P	50 - 5000	—
Pb	2.0 - 200	0.1 - 3000
Ra	$10^{-6.5}$ - $10^{-5.7}$	—
Rb	20 - 600	3.0 - 3000
S	30 - 10,000	—
Sb	0.6 - 10	—
Sc	10 - 25	—
Se	0.1 - 2.0	0.01 - 400
Si	230,000 - 350,000	—
Sn	2.0 - 200	0.1 - 700
Sr	50 - 1000	10 - 5000
Th	0.1 - 12	—
Ti	1000 - 10,000	400 - > 10,000
U	0.9 - 9.0	< 250
V	20 - 500	1.0 - 1000
Y	10 - 500	—
Zn	10 - 300	3.0 - 10,000
Zr	60 - 2000	10 - 8000

[a] Based on an Analysis of Data Presented in References 1,2,3,4,5, and 6.

- Leaching of mobilized elements such as calcium, boron, lithium, iron, magnesium, manganese, selenium, or sodium (a) out of the soil profile, or (b) into zones of accumulation.
- Translocation, in the course of soil-forming processes such as podzolization, of trace elements together with iron and aluminum.
- Mobilization of trace elements through breakdown of soil minerals as a result of alternate wetting and drying.
- Mechanical translocation of clay, which increases trace element concentrations in those soil horizons having higher amounts of clay particles.
- Surface accumulation of relatively soluble elements such as boron, calcium, and sodium in arid regions.
- Mobilization or fixation arising from chemical and/or microbiological activity.
- Surface enrichment due to trace element uptake by plants.

Second, analytical data derived from the chemical analysis of the total element content of a soil (i.e. C_{Total}) relays no information regarding C_{Fixed}, $C_{Adsorbed}$, and C_{Water} other than the magnitude of their combined concentrations. In other words, if a laboratory report states that a soil contains 125 ppm total Cu, this datum cannot reveal if 0.1 percent is potentially mobile (i.e. $C_{Adsorbed} + C_{Water}$) or if 99 percent is potentially mobile. At background concentrations, the relative magnitudes of the parameters listed in Equation 3.1 for cations generally are:

$$C_{Fixed} >> C_{Adsorbed} > C_{Water}$$

The greater part of C_{Total} exists as C_{Fixed} and is immobile. However, this relative ranking may or may not change as C_{Total} increases above the background concentration.

Third, the background concentrations listed in Table 3.1 represent the total concentration of an element present after the soil was formed and weathered. This concentration gives no information on the element-loading capacity of a soil. The element-loading capacity can be defined as the maximum amount of an element that can be added to soil which does not cause water migrating through this soil to contain a harmful concentration of that element. In other words, knowing that a soil contains 125 ppm total background Cu will not reveal if soil will or will not completely convert an additional loading of 500 ppm Cu into C_{Fixed}.

Soil cleanup standards that specify the excavation or treatment of soil containing concentrations of an element over a background concentration are usually based on an incorrect premise that the background concentration of an element in soil represents a maximum concentration of an element which the soil can immobilize. The background concentration represents the total concentr[illegible] present after the soil was formed and undergone some degree

TABLE 3.2 Natural Concentrations of Various Elements in Groundwater.[a]

	Concentration	
Element	*Typical Value*	*Extreme Value*
	Major Elements (ppm)	
Ca	1.0 - 150[b]	95,000[c]
	< 500[d]	
Cl	1.0 - 70[b]	200,000[c]
	< 1000[d]	
F	0.1 - 5.0	70
		1600[c]
Fe	0.01 - 10	> 1000[c,e]
K	1.0 - 10	25,000[c]
Mg	1.0 - 50[b]	52,000[c]
	< 400[d]	
Na	0.5 - 120[b]	120,000[c]
	< 1000[d]	
NO_3	0.2 - 20	70
SiO_2	5.0 - 100	4,000[c]
SO_4	3.0 - 150[b]	200,000[c]
	< 2000[d]	
Sr	0.1 - 4.0	50
	Trace Elements (ppb)	
Ag	< 5.0	
Al	< 5.0 - 1000	
As	< 1.0 - 30	4,000
B	20 - 1000	5,000
Ba	10 - 500	
Br	< 100 - 2000	
Be	< 10	
Bi	< 20	
Cd	< 1.0	
Co	< 10	
Cr	< 1.0 - 5.0	
Cu	< 1.0 - 30	
Ga	< 2.0	
Ge	< 20 - 50	
Hg	< 1.0	
I	< 1.0 - 1000	48,000[c]
Li	1.0 - 150	
Mn	< 1.0 - 1000	10,000[c]
Mo	< 1.0 - 30	10,000
Ni	< 10 - 50	
PO_4	< 100 - 1000	
Pb	< 15	
Ra	< 0.1 - 4.0[f]	720[c,f]
Rb	< 1.0	
Se	< 1.0 - 10	
Sn	< 200	
Ti	< 1.0 - 150	
U	0.1 - 40	
V	< 1.0 - 10	70
Zn	< 10 - 2000	
Zr	< 25	

[a] based on an analysis of data presented in references 7,8, and 9.
[b] in relatively humid regions.
[c] in brine.
[d] in relatively dry regions.
[e] in thermal springs and mine areas.
[f] picocuries/liter (i.e. 0.037 disintegrations/sec).

of weathering; it gives no indication of the maximum concentration of an element which a soil can immobilize, i.e., the element loading capacity of the soil.

Fourth, a number of established, accepted laboratory methods exist for determining the magnitude of C_{Total}, C_{Fixed}, $C_{Adsorbed}$, and C_{Water} in soil. C_{Total} is usually measured by dry ashing at 500 to 550°C for 3 to 4 hours or by wet ashing with a mixture of perchloric and nitric or sulfuric acids. $C_{Adsorbed}$ and C_{Water} are usually determined by using mineral acids (e.g. 0.1 N HCl), organic acids, and chelating agents (e.g. EDTA, DTPA); hot water extractions as usually utilized for elements that exist as anions (e.g. B, Mo, Se). It is most important to note that the test method employed is dependent upon the individual element to be tested, the parameter to be tested (e.g. C_{Fixed} versus $C_{Adsorbed}$), and the soil type. There is no "universal" analytical method which is applicable for all forms of an element in all soils.

It is most important to note that there are test methods, which are similar to the ones mentioned above, that are utilized to determine the amount of extractable chemical from wastes; these are used to determine if the waste should be classified as a hazardous waste and must be disposed in a Class I landfill. These test methods include the U.S. EPA's EP Toxicity, the TCLP test method, and the State of California's CAM-WET procedure (California Assessment Manual - Wet Extraction Procedure). These methods should not be utilized for soil cleanup criteria from spills of hazardous materials for two reasons. First, these methods, when applied to soils, provide a value, $C_{Extract}$, where:

$$C_{Extract} = a\,C_{Fixed} + b\,C_{Adsorbed} + C_{Water} \tag{3.2}$$

where:

$C_{Extract}$ = concentration of an element extracted from a soil; $C_{Total} > C_{Extract}$

a, b = fractions

Since a and b are not determined, it is not possible to relate the parameters of Equation 3.2 to those of Equation 3.1. In other words, $C_{Extract}$ provides no information regarding the magnitude of C_{Fixed}, $C_{Adsorbed}$, and C_{Water}, information which is needed to determine the potential migration and transformation of an element in soil.

Second, when soils are exposed to the extractants utilized by these test methods (acid and citrate or acid and acetate), gross alterations can occur in soil mineralogy, in naturally occurring soil chemical reactions, and in soil physical and chemical properties. These gross alterations result from the fact

that the extractants can (a) selectively dissolve soil minerals, (b) impede crystallization and formation of aluminum hydroxides and other soil minerals while causing structural distortions in newly formed minerals, (c) perturb hydrolytic reactions of aluminum, and (d) desorb, via mass action, elements and organics from soil adsorption sites which may not normally be desorbed. Because the extractants cause gross alterations in the chemical and mineralogical properties of soil systems, the data derived from these test methods, when soil is utilized as the solid phase, cannot be extrapolated to actual field conditions. Therefore, they should not be used for soil cleanup criteria from spills of hazardous materials.

The cleanup of contaminated soil should be engineered on a case-by-case basis using published and appropriate soil testing methods; the scientific literature contains at least seven test methods addressing the leaching potential of chemicals in soils[10], and numerous methods addressing the biological, chemical, and physical properties of soils[11,12,13,14].

ELEMENT FIXATION IN CLAY AND SOIL MINERALS

The quantity C_{Fixed} in Equation 3.1 was defined as the concentration of fixed element which has been incorporated into the structure of clay and soil minerals. This section of Chapter 3 will discuss how an element that enters a soil system can be immobilized by fixation into the structure of clay and soil minerals.

Some chemicals such as HCl and water are miscible in all proportions. In other words, continual additions of HCl into a beaker filled with water will not result in the precipitation of a solid in a beaker nor the formation of a separate phase of HCl. For most chemicals, however, there is a limit to the amount that can be added before a solid will precipitate. For example, when a small amount of $MgCO_3$ is added to water, it dissolves. As more $MgCO_3$ is added, it dissolves. However, a point will be reached where additions of $MgCO_3$ will not dissolve but will settle at the bottom of the beaker as a crystalline solid. An equilibriuim is established in which the rate of precipitation of $MgCO_3$ (solid, s) equals the rate of dissolution of $MgCO_3$ (s) into dissolved Mg^{2+} and CO_3^{2-}:

$$Mg^{2+} + CO_3^{2-} \underset{\text{Dissolution}}{\overset{\text{Precipitation}}{\rightleftharpoons}} MgCO_3\ (s) \tag{3.3}$$

Now suppose that in addition to Mg^{2+} and CO_3^{2-}, dissolved Ni^{2+} was also present in water at a concentration equal to that of dissolved Mg^{2+}. Ions such as Ni^{2+} which have the same valence and similar size as Mg^{2+} can replace Mg^{2+} in the crystal structure of the precipated structure. In other